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## SPECTROGRAPHIC ANALYSES OF PALEOZOIC BLACK SHALE SAMPLES

By

## James D. Vine

This report consists of the tabulated spectrographic analyses of 220 black shale samples divided into four sets on the basis of geography, sample type, and age of rocks represented. Chemical analyses for carbon are included for most samples.

Set No. 1 consists of core samples of black shale from the Tradewater and Carbondale Formations of Pennsylvanian age, recovered from four bore holes drilled by the U.S. Geological Survey in the vicinity of Owensboro, Ky.

Set No. 2 consists of samples of black shale from outcrops and artificial exposures of the Tradewater and Carbondale Formations in the Western Kentucky Coal Field extending from the vicinity of Owensboro south to the vicinity of Madisonville.

Set No. 3 consists of thin splits from a single bed of black shale and coaly shale from a shallow quarry in the Linton Formation of Pennsylvanian age near Mecca, ind.

Set No. 4 consists of samples from widely scattered exposures of Ordovician and Silurian rocks in California, Nevada, Idaho, Washington, and British Columbia. These samples are chiefly siliceous black shale from the graptolitic shale facies of the western North American eugeosyncline termed the Frazer Belt by Kay (1947). This facies in Nevada is in what Roberts and others (1958, p. 2817) called the western and transitional assemblages, which were deposited to the west of the early Paleozoic Cordilleran miogeosyncline.

The samples in the first three sets are chiefly grayish black to black clay shales and coaly shales, containing only a minor quantity of detrital silt, and an unusually large amount of organic matter, as indicated by the analyses for organic carbon (or total carbon, where carbonate carbon was insignificant). Fish scales and fins and inarticulate brachiopods are abundant in some beds and locally these have been pyritized. The samples represented by Sets No. 1 and No. 2 from the Western Kentucky Coal Field were collected so as to include a black shale bed equivalent to that from western Indiana, as well as several additional beds stratigraphically above and below in adjacent cyclothems. Set No. 3 from western Indiana is unusual, in that it represents the variation within 37 samples split from a single bed of black shale I foot thick. The detailed stratigraphy, paleontology, and ecology of this bed were described by Zangerl and Richardson (1963), who. first investigated the shale because it contained a rich vertebrate fauna (chiefly fish) in association with invertebrates.

Set No. 4 includes a wider variety of lithic types than the first three sets, ranging from grayish black to black siliceous mudstone and siltstone to dark gray calcareous shales. Graptolites are characteristic fossils and are locally abundant; they generally are preserved as carbonaceous films, although pyritized graptolites are rarely present. Carbon analyses are not available for many of the samples in Set No. 4, but in general, these samples probably contain less organic carbon than samples from the other three sets. Efforts were made to obtain fresh sample material, but some of the samples in Set No. 4 show obvious signs of bleaching and other effects of weathering in a desert climate.

The tabulated data in each set are reproduced directly from the machine print-out of the U.S. Geological Survey's geochemical data coding and retrieval cards in order to minimize the chances for error. The numerical data are accompanied by brief locality and sample descriptions, also in tabular form.

Persons using and interpreting these data should bear in mind that the four sets of data are not directly comparable in several significant respects. Some pertinent differences are indicated in the following table.

Set No.	Num Sam- ples	ber of Locali- ties	Area or region	Sample description (generalized)	Age	Depositional environment
1	66	4	Western Kentucky	0.5 ft coaly shale, core	Pennsyl- vanian	Transgressive brackish or marine, shelf
2	42	20	do	0.75 ft coaly shale, outcrop	do	Do.
3	37	1	Indiana	0.02 ft coaly shale, quarry	do	Do.
	75	51	Western North América	1.0 ft siliceous shale, outcrop	Ordovi- cian and Silurian	Eugeosyncline (abyssal slope)

The approximate lower limits of detection for elements determined by the six-step spectrographic method are as follows:

Si	0.002	K (	0.7	Ba	0.0002	La	0.002	V	0.001
Al	.001	Ti	.0002	Вe	.0001	Мо	.0005	Y	.001
Fe	.0008	P	.2	Co	.0005	Ńi	.0003	Zn	.02
Mg	.0005	Mn	.0002	Cr	.0001	Рb	.001	Zr	.001
Ca	.005	Ag	.0001	Cu	.0001	Sc	.0005		
Na	.05	В	.002	Ga	.0002	Sr	.0002		

A statistical summary and geochemical interpretation of the data tabulated here will be published at a later date. Subsequent reports will include analyses of other black shale sets.

Many individuals contributed directly or indirectly to the collection and analysis of the samples and to the processing of the data. In particular, I wish to thank Rainer Zangerl for donating the samples in Set No. 3 from his collections at the Chicago Natural History Museum, R. H. Calvert, J. E. Palmer, and T. M. Kehn for their aid in collecting the samples in Sets No. 1 and No. 2, and J. P. Alberts, Michael Churkin, Jr., R. R. Coats, K. B. Ketner, F. J. Kleinhampl, R. J. Roberts, D. C. Ross, J. F. Smith, Jr., and R. G. Yates for their aid in collecting the samples represented by Set No. 4. Spectrographic analyses of samples were made in the laboratories of the U.S. Geological Survey in Menlo Park, Calif., by Chris Heropoulos under the direction of Harry Bastron, and in Denver, Colo., by J. C. Hamilton and A. L. Sutton, Jr., under the direction of A. T. Myers. Carbon analyses were made by I. C. Frost, in the Denver laboratory, under the direction of L. F. Rader. Mary S. Niles was in charge of transcribing the analytical data to the data coding and retrieval cards, and Ralph Eicher provided the machine print-out of the data from the punched cards.

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